[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COPENHAGEN.]

A REACTION BEWEEN METHYL ALCOHOL AND WATER AND SOME RELATED REACTIONS.

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In experiments on the synthesis of methyl alcohol I had observed that a mixture of steam and methyl alcohol vapor when passed through finely divided reduced copper reacts with the formation of hydrogen and carbon dioxide. To follow up this interesting reaction, I made some further experiments showing that the reaction

$$CH_3OH + H_2O = CO_2 + 3H_2 \qquad (1)$$

proceeds sensibly without side-reactions.

The reduced copper was made from copper oxide precipitated from a hot solution of copper sulfate by means of sodium hydroxide, and was contained in a vertical U-tube (of combustion glass about 20 cm. in height and 10 mm. in diameter, that could be heated in an oil-bath to about 300°. The upper end of one branch was bent in an angle of about 45°, while the upper end of the other was bent to a horizontal position.

From a buret a mixture of methyl alcohol and water was passed through the inclined tube. The velocity of the stream was regulated by a capillary through which it was forced by means of an air pressure of several centimeters of mercury. The horizontal tube was connected with a vertical cooling coil which served to condense the vapors of water, methyl alcohol, and other condensable compounds that passed over. The condensate was collected in a small suction flask with side-tube. From this the gases passed to two spiral absorption tubes containing sodium hydroxide to absorb the carbon dioxide. The non-absorbed gases were finally collected over water in a calibrated gas buret of 500 cc. capacity.

Between the suction flask and the absorption tubes a T-form stopcock was inserted, the free end of which dipped under water in a cylinder. By means of this device it was possible to sweep out the air of the suction flask, and to start and stop the collection of the gases at any given moment. Simultaneously the height of the liquid in the buret was noted, and so the quantity of alcohol solution, delivered during the period, was known.

In each experiment the quantities of carbon dioxide and formic acid (plus methyl formate) were determined by titration, the former according to Winckler's method. The mixture in the gas buret was analyzed by means of an Orsat apparatus.

As the air in the suction flask was displaced by the carbon dioxide-hydrogen mixture before the beginning of the experiment, the volume of hydrogen formed was found by subtracting the volume of diluted

alcohol used from the volume of gas collected, subject to a correction because the air was not totally displaced, and determined by the difference between the air found by analysis and the known volume of the air space in the absorption tubes. This was applied by subtracting $^1/_4$ of the difference from the volume of hydrogen found. Of course all volumes were properly corrected for the influence of varying temperature, pressure and moisture content.

Only traces of free acid and carbon monoxide were found.

From these data the molecular proportion between the hydrogen and carbon dioxide formed during the reaction was calculated. In the first experiments this proportion was constantly found at about 2.8, but it appeared that the deviation was due to a piece of rubber tubing, several centimeters in length, inserted between the last absorption coil and the gas buret, through which the hydrogen diffused in spite of the fact that it was completely immersed in water. When this tubing was replaced by a glass tube, the proportion became exactly 3, indicating that the reaction proceeds practically without side reactions according to Equation 1.

The following is a typical experiment.

The alcohol (about 99%) was diluted 1 to 10 by volume. The temperature of the oil-bath was 255° ±1°. During 108 minutes 20.00 cc. of the liquid passed the apparatus.

	Cc.
Volume of gas collected, reduced to standard conditions, dry,	283.6
Correction for distillate	17.7
Correction for air displaced by CO_2	0.7
Volume of hydrogen found	265.2
CO_2 found	
In 20 cc. of distillate	4.0
In the second absorption tube	1.1
In the first absorption tube	82.5
In gas (?)	0.5
Volume of carbon dioxide	88.1
Volume of hydrogen / Volume of carbon dioxide	3.01

Later it was found that formaldehyde also is hydrolyzed according to the analogous reaction

$$CH_2O + H_2O = CO_2 + 2H_2, \qquad (2)$$

at a temperature of about 235° and with finely divided copper as a catalyst, but the experiments were of a more qualitative nature.

It is very probable that some of the hydrogen is used up in reduction of formaldehyde to methyl alcohol, so that the proportion of hydrogen to carbon dioxide will be smaller than 2, a result also indicated by the above experiments.

In this connection it may be of interest to note that the well known reaction

$$HCOOH = CO_2 + H_2$$

catalyzed by copper, according to an experiment of mine also proceeds with formation of an excess of carbon dioxide, presumably on account of reduction of formic acid.[1]

Summary.

Experiments are reported showing that the reactions $CH_3OH + H_2O = CO_2 + 3H_2$ and $CH_2O + H_2O = CO_2 + 2H_2$ proceed when suitable vapor mixtures are led through finely divided reduced copper at temperatures about 230° to 250°.

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[CONTRIBUTION FROM THE ABBOTT LABORATORIES.]

PREPARATION AND HYDROLYSIS OF BENZYL ESTERS.

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In his classical researches on the therapeutic properties of combined opium alkaloids, and particularly of the alkaloids of the papaverine group, Macht[1] found that the antispasmodic effect of these compounds is due to the benzyl nucleus. This discovery was followed by his investigation of two simple organic esters of benzyl alcohol, namely, benzyl acetate and benzyl benzoate. It was found that the former is undesirable due to gastric disturbances which it induces, whereas benzyl benzoate is quite effective in relaxing unstriped muscle, and is better tolerated than benzyl acetate.

Up to the present time benzyl benzoate is the only benzyl ester which has come into extended use, although benzyl stearate and benzyl succinate have recently been introduced. The chief obstacle in studying new benzyl esters is the difficulty of determining the relative merits of the various esters by any methods that are rapid and fairly accurate. The general insolubility of the esters in water makes pharmacological tests difficult. Hence, in determining the comparative values of new benzyl esters, actual clinical use has always been necessary in spite of the length of time and of the uncertainties incident to such examinations.

A rapid chemical method of gaining a preliminary idea of the value of these esters would be extremely desirable. In devising such a test, it would be necessary to know whether the effect of benzyl esters is due to the entire benzyl ester molecule or to benzyl alcohol formed by hydrolysis of the ester in the body. The fact that benzyl benzoate and benzyl

[1] Cf. Sabatier, "Die Katalyse in der organischen Chemie," Leipzig, **1914**, p. 151.

[1] Macht, *J. Pharmacol.*, **9**, 287 (1917); **11**, 389–446 (1918).